PR-3. COMPUTATIONAL MODELING OF SOLVENT EFFECT ON FLUORESCENCE SPECTRA. IMPLICATIONS TO THE FLUORESCENT STATE STRUCTURE

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The observed shifts of the electronic absorption and emission bands of organic compounds induced by solvents are commonly understood as an indication of the extent of charge reorganization upon electronic excitation, respectively radiative excited state deactivation. Our computational model for prediction of the energies of the electronic (absorption and fluorescence) transitions of organic molecules, as well as their solvent dependence is based on part of the Jablonsky diagram and includes explicit geometry optimization of the S_0 and S_1 electronic states in different solvents. On the basis of reasonable success in accounting for the observed solvent effects on the electronic spectra of several classes of chromophores we consider this methodology also suitable for the lowest molecular excited state structures as well.

Methyl-2,3-dihydroquinolinones exhibit large solvent dependence of their fluorescence maxima, shifted bathochromically by ca. 5600 cm^{-1} on passing from hexane to water. Two different correlations of the experimental energies of the fluorescence maxima versus calculated values are found. The solvent effects in aprotic solvents are consistent with continuum type solvent-solute interactions, while in protic solvents the existence of solvent-solute complexes is indicated by both experiment and computations. The estimated additional stabilization of the S_1 state due to hydrogen bonding with the solvent is around 2300 cm^{-1}.

PRODAN is one of the best known highly sensitive fluorophores and is used extensively as a fluorescent probe for micropolarity in various chemical and biological systems. Separate linear regressions for aprotic and protic solvents, respectively, between the experimental and calculated energies of the emission maxima have drastically different slopes and much higher correlation coefficients than the respective common relationships including all solvents. This observation is in agreement with the deduction derived from experimental data that the nature of the emitting state in protic and aprotic solvents is different, presumably due to hydrogen bonding of PRODAN in the S_1 state with protic solvents. The additional stabilization energy of the S_1 state in protic solvents is ca. 2000 cm^{-1}. On the basis of our computational results we further address the nature of the lowest excited singlet state, S_1. The results support the concept that no geometry twist in the S_1 state is necessary to explain the observed solvent effects on fluorescence.

2-[2′-hydroxyphenyl]-quinazolin-4-one, HPQ, is capable of keto-enol tautomerism, not directly indicated by the electronic spectra. We look for additional DFT and TD-DFT computational, as well as experimental, insight into the spectroscopic properties of HPQ. The results indicate the simultaneous presence of enol and keto forms both in the ground and first excited singlet state, as well as ESIPT giving rise to overlapping fluorescence emissions.

The financial support of the National Science Fund of Bulgaria (Contract DN 19/11, 10.12.2017) is gratefully acknowledged.